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DEPARTMENT OF PHYSICS
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OLD DOMINION UNIVERSITY
NORFOLK, VIRGINIA

Technical Report PTR-82-2

THEORETICAL STUDIES OF SOLAR-PUMPED LASERS

By

Wynford L. Harries, Principal Investigator

Progress Report
For the period July 16, 1981 - January 15, 1982

Prepared for the
National Aeronautics and Space Administration
Langley Research Center
Hampton, Virginia

Under
Research Grant NSG 1568
John Wilson, Technical Monitor
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THEORETICAL STUDIES OF SOLAR-PUMPED LASERS

By

Wynford L. Harries*

SUMMARY

This report summarizes work performed under NASA grant No. NSG 1568 during the period from July 16, 1981 to January 15, 1982. Two important problems concerning solar-pumped lasers were investigated:

(1) Comparing experimental results from pulse experiments with steady-state calculations. "Time Varying Behavior of an IBr Laser" presents a simple analysis which takes account of the behavior vs. time. The analysis is only approximate, but indicates that conditions occurring in a pulsed experiment are quite different from those at steady state.

(2) Determining whether steady-state lasing is possible in an IBr laser. This requires examining the effects of high temperatures on the quenching and recombination rates. Although uncertainties in the values of the rate coefficients make it difficult to draw firm conclusions, it seems steady-state running may be possible at high temperatures.

LIST OF SYMBOLS

A_1	unit cross section
C	number of times the solar radiation has been concentrated
c	velocity of light
ΔG	free energy
D	dissociation constant

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d	depth of laser
h	Planck's constant
k	Boltzmann's constant
$k_1, k_2, k_3, k_4, k_5, k_6, k_7$	quenching rate coefficients
k_T	quenching rate vs. temperature
ℓ	absorption length
n	number of passes through the gas
p	pressure, torr
S_1	production rate
S_1'	source term
T	temperature, Kelvin
t	time
x	position
α	temperature effect
β	function of α
κ	conductivity
λ	wavelength
$\Delta\lambda$	bandwidth
λ_a	λ at peak absorption
ρ	gas density
ρC_v	heat capacity
σ_a	cross section
ν	frequency
$\phi(\lambda)$	solar radiance

TIME-VARYING BEHAVIOR OF AN IBr LASER

The purpose of this analysis, which is approximate, is to illustrate the difference between a pulsed and a steady-state IBr solar-pumped laser. We shall consider variations with time, but assume lasing does not occur, and estimate whether inversion is possible.

A flow chart for the processes occurring in an IBr solar-pumped laser is shown in figure 1. The IBr pressure is assumed sufficiently great so that almost all of the incoming radiation is absorbed, each photon of which dissociates the IBr into I + Br*. If complete mixing of the Br* occurs through the volume, the rate of production of Br* is $\frac{C\phi\Delta\lambda_a}{d}$ where C is the number of times the solar radiation has been concentrated, $\phi(\lambda)$ is the solar radiance in photons ($cm^{-2}s^{-2}A^{-1}$), and $\Delta\lambda_a$ the absorption bandwidth in A. If quenching by IBr dominates the loss processes just prior to attaining inversion, then the rate equation for Br* is approximately

$$\frac{dBr^*}{dt} = \frac{C\phi\Delta\lambda_a}{d} - k_1 Br^*(IBr) \tag{1}$$

where k_1 is the quenching rate coefficient.

Neglected are quenching by I_2, Br_2, and He which may be present. The amounts of I_2 and Br_2 present should be small because they are photodissociated and quenching by He is probably negligible. Three-body recombination of Br* with I and spontaneous emission are also assumed negligible compared with the quenching.

The rate equation for Br is approximately

$$\frac{dBr}{dt} = k_1 Br^*(IBr) - k_6(I)(Br)(IBr) - k_8 Br(IBr) - k_9 Br(IBr)^2 \tag{2}$$
$$- k_{10} Br(IBr)He$$

The Br is produced by quenching Br* with IBr. Neglected are the rates for Br* quenched by I_2, Br_2, and He for the same reasons as above. Three-body

recombination occurs with a rate coefficient k_6. The last three terms represent exchange reactions which remove Br by forming Br_2. The first suggestion for including exchange reactions was made by W. Meador (ref. 1), who pointed out the reaction

$$Br + 2IBr \xrightarrow{k_9} I + Br_2 + IBr \; ; \; k_9 = 10^{-30} cm^6 s^{-1}$$

This reaction is three-body. A two-body exchange reaction was described by Clyne and Cruse, who claimed they had measured the rate coefficient for the reaction (ref.2):

$$Br + IBr \xrightarrow{k_8} I + Br_2; \; k_8 = 3.5 \times 10^{-11} cm^3 s^{-1}$$

However, doubt exists whether this exothermic reaction is possible, as 0.2 eV of energy has to be removed. It will be shown later that the high value of k_8 is not compatible with measurements of k_1 as $k_1 - k_8$ has to be positive.

If the three-body exchange process with IBr as the third body is possible, then it is suggested that, if an appreciable amount of He is present, the exchange process:

$$Br + IBr + He \xrightarrow{k_{10}} Br_2 + I + He; \; k_{10} \approx 10^{-30} cm^6 s^{-1}$$

where the value of k_{10} is guessed. Recombination where the third body is I_2, Br_2, or He is neglected.

Equation (1) yields the approximate time behavior of Br*:

$$Br^* \simeq \frac{C\phi\Delta\lambda_a}{dk_1(IBr)} \left\{ 1 - \exp\left[- k_1(IBr)t\right] \right\} \tag{3}$$

For small t,

$$Br^* = \frac{C\phi\Delta\lambda_a t}{d}; \text{ t small} \tag{4}$$

and for large t, the Br* reaches a saturation level independent of time:

$$Br^* = \frac{C\phi\Delta\lambda_a}{dk_1\ (Br)}\ ; \text{ t large} \tag{5}$$

For small t, the first term on the right in equation (2) will dominate. By neglecting all other terms, and integrating using equation (4), then

$$Br \approx \frac{k_1(IBr)C\phi\Delta\lambda_a t^2}{2} \tag{6}$$

Thus, the inverted population Br* - Br/2 is given by:

$$Br^* - \frac{Br}{2} = \frac{C\phi\Delta\lambda_a}{d}\left(1 - \frac{k_1(IBr)t}{4}\right)t \tag{7}$$

The equation is very approximate and the function $Br^* - \frac{Br}{2}$ is represented by a parabola displaced from the origin. The quantity $Br^* - \frac{Br}{2}$ grows with time, but then decreases to zero in a time of order $\frac{4}{k_1(IBr)}$. Assuming $k_1 = 10^{-12}\ cm^3 s^{-1}$ (ref. 3) and a pressure of 10 torr, the calculated time is of order 20 μs, somewhat smaller than the observed experimental times of 45μs.

Despite the approximation, the result is included here as it clarifies one important aspect: On the above assumptions the population of the lower laser level, Br, is formed from Br*, which fills up first. Equations (4) and (6) show $Br^* \propto t$, and $Br \propto t^2$, so for small t, $Br^* > Br$.

The above analysis is an oversimplification and, as equation (2) is nonlinear, the set was solved by computer and plotted graphically in figure 1. The values assumed are $C = 10^4$, $k_1 = 10^{-12} cm^3 s^{-1}$, $k_6 = 3 \times 10^{-30} cm^6 s^{-1}$, and $k_8 = 0$ (for reasons to be explained later). The corresponding IBr pressures are 1, 3, and 5 torr respectively. In figures 1(a) and (b), no He is present; in figures 1(c) and (d), 30 torr of He is added. The plots show

the inverted population $Br^* - \frac{Br}{2}$ vs. time and slightly different values of k_9 are assumed. In figures 1(a) and (c), k_9 is assumed to be 10^{-30}, and in figures 1(b) and (d), k_9 is assumed to be 3×10^{-30} $cm^6 s^{-1}$. Cases (a) and (c) show that an inverted population would be maintained for a duration many tens of μs, but cases (b) and (d) show that the ordinate stays positive as time increases. Evidently the value of k_9 is critical, but steady-state running may be possible.

The requirement $Br^* - \frac{Br}{2} > 0$ is a necessary but not sufficient condition for lasing. The curves should bear little relation to the time behavior of the laser light, as the loss of Br* by stimulated emission is omitted. The laser light profile would, however, be contained in time, within the regions the curves are positive, and it seems steady-state lasing is at least possible. Also, in a pulsed experiment it may be possible to get lasing, although lasing would not occur in the steady state. In the experiments at NASA with $C = 10^4$ (ref. 4), the laser pulses were of about 45-μs duration at 1.5, 3, and 5 torr of IBr and almost independent of pressure. The times when the inverted population could exist, shown in figure 2, agree in order of magnitude.

Care must be taken in comparing pulsed and steady-state conditions. If steady-state running cannot be achieved, then one possibility is to consider Q-switched lasers, where the input is continuous, and the output pulsed. The possibility of attaining a steady state is examined in the next section.

TEMPERATURE EFFECTS IN SOLAR-PUMPED LASERS

Introduction

The purpose of this section is to examine the possibility of running a steady-state IBr laser. The new aspect to be considered is the effect of high temperatures on the various rate coefficients, as high temperatures will occur anyway for high solar concentrations. The parameters of the laser are also checked for compatibility with reasonable mechanical construction.

The physical mechanism and condition for inversion are discussed under "Physical Processes of the Laser." The temperature of the lasing gas is then calculated (see "Gas Temperature in an IBr Laser"), followed by a discussion of its effects on quenching, dissociation, and recombination ("Effect of Temperature on the Rate Coefficients"). The population inversion condition for various temperatures is examined under "Speculations on a Steady-State IBr Laser."

Physical Processes in the Laser

General. - A flow chart for an IBr + He solar-pumped laser is shown in figure 2. The He is introduced to increase the three-body recombination of the lower level, Br, and yet have a low quenching cross section for Br*. The IBr is dissociated by the photons so that the rate of production of Br* per unit volume is S_1(IBr) where (IBr) is the molecular density. The Br* is quenched by IBr, He, and I_2 with rate coefficients k_1, k_2, and k_3. It also recombines with I where IBr and He act as third bodies, with coefficients k_4 and k_5. The Br, representing the lower laser level, is created if Br* is quenched, spontaneously emits (the rate is negligible), or if lasing occurs. It is removed by recombination with I where IBr or He acts as a third body with rate coefficients k_6 and k_7, respectively, and by the exchange reactions mentioned earlier ("Time-Varying Behavior of an IBr Laser") with coefficients k_8, k_9, and k_{10}.

Numerous approximations have been made, as the intent here is to obtain results correct in order only It is assumed that the densities of IBr and He will be much greater than those for I_2 and Br_2. I and Br will be created by thermal dissociation at high temperatures and then will recombine to form IBr, I_2, Br_2. The error in neglecting the effect of I_2 and Br_2 as third bodies would be expected to be small. However, quenching by I_2 should be included, as at room temperature the rate coefficient for I_2 is 60 times greater than for IBr.

The rate equations for Br* and Br are

$$\frac{dBr^*}{dt} = S_1(IBr) - k_1Br^*(IBr) - k_2Br^*(He) - k_3Br^*(I_2) \tag{8}$$
$$- k_4Br^*I(IBr) - k_5Br^*(I)(He) - A_eBr^*$$

$$\frac{dB}{dt} = S_2(IBr) + k_1Br^*(IBr) + k_2Br^*(He) + k_3Br^*(I_2)$$
$$- k_6Br(I)(IBr) - k_7Br(I)(He) + A_eBr^* - k_8Br(IBr)$$
$$- k_9Br(IBr)^2 - k_{10}BrHe \tag{9}$$

The S_2 source term represents the reaction $h\nu + IBr \rightarrow Br + I$, and, for IBr, S_2 is approximately zero. The Einstein coefficient $A_e \approx 1$ and spontaneous emission is negligible.

We shall consider the case where inversion just becomes possible, because this can be solved simply. Inversion is just possible when

$$B^* > \frac{Br}{2} \tag{10}$$

The factor 2 enters because the B* is in a $^2P_{1/2}$ state with a degeneracy of 2, while the Br is in a $^2P_{3/2}$ state with a degeneracy of 4. The condition for inversion is less stringent than for lasing, which requires finite gain to overcome laser losses. It is a necessary but not sufficient condition for lasing; but if not satisfied, lasing is impossible. The calculation avoids the inclusion of stimulated emission, which has not started yet. A quasi-static condition is envisaged with C slowly increased; hence steady-state conditions are assumed.

<u>The absorption process</u>. - The source term of Br*, $S_1(IBr)$, is calculated assuming an absorption cross section $\sigma_a(\lambda)$ constant over a bandwidth $\Delta\lambda_a$ and zero outside the bandwidth. The effect of $\sigma_a(\lambda)$ being a Gaussian is considered later. Assuming that the number of photons absorbed between a depth x and $x + dx$ is proportioned to σ_a, and to the density of the

absorber (IBr), then the intensity of radiation in the absorber will decay exponentially with an absorption length $\ell = ((IBr)\sigma_a)^{-1} = 100/p$ where p is the IBr pressure in torr. Assuming that the Br* undergoes complete mixing and its density is approximately constant throughout the volume, then the rate of production of Br* per unit volume is

$$\frac{dBr^*}{dt} = \frac{C\phi(\lambda)\Delta\lambda_a}{d} \; 1 - \exp\frac{-nd}{\ell} \tag{11}$$

The quantity n is the number of passes through the gas; a reflector on the far side (n = 2) would help considerably in getting an even distribution of Br*. For example, for n = 2 and ℓ = d, the variation in $\frac{dBr^*}{dt}$ throughout the volume, even if there were no mixing, would be about 30 percent.

In the case of $\ell \gg nd$ and the exponent small, equation (11) shows

$$\frac{dBr^*}{dt} \simeq nC\phi\Delta\lambda_a\sigma_a(IBr) \tag{12}$$

The cross section σ_a equals $\frac{\lambda_a^4 A_{13}}{4\pi^2 c\Delta\lambda_a}$ where A_{13} is the Einstein coefficient for the transfer from level 1 to level 3 of the laser, λ_a the wavelength at peak absorption, c the velocity of light, and $\Delta\lambda_a$ the absorption bandwidth as before. In this case

$$\frac{dBr^*}{dt} = \frac{nC\phi\lambda_a^4 A_{13}(IBr)}{4\pi^2 c} \; ; \; \ell \gg nd \tag{13}$$

independent of $\Delta\lambda_a$ and d, the case of an optically thin absorber. Few

photons are absorbed per unit distance, and $\frac{dBr^*}{dt}$ is roughly constant with position x. The geometry of the solar laser is described by n and C, the ratio of reflector to absorber cross section. The absorbing material is described by λ_a, which determines the magnitude of $\phi(\lambda)$, and A_{13}. Increasing the pressure (IBr) increased the rate.

If $\ell \ll nd$, then equation (11) shows

$$\frac{dBr^*}{dt} = \frac{C\phi\Delta\lambda_a}{d} \; ; \; \ell \ll nd \tag{14}$$

All the photons are now absorbed. The rate of absorption is high on the near side, and approaches zero on the far side of the absorbing vessel. The redistribution of Br* by diffusion and/or mixing over a distance d is assumed, so equation (14) gives an average value.

The production rate is now independent of the pressure and, to be consistent with equation (1), we define a new source term, $S_1'(IBr)$:

$$S_1'(IBr) = \frac{C\phi\Delta\lambda_a (IBr)}{d(IBr)} \tag{15}$$

and the ratio of the two source terms is

$$\frac{S_1}{S_1'} = nd\sigma_a(IBr) = \frac{npd}{50} \tag{16}$$

The quantity npd is proportional to the total number of absorbing atoms a photon would meet in crossing the vessel n times and a similarity law is obeyed.

In actual practice it would be expected that the conditions would be intermediate between S_1 and S_1'. To obtain appreciable absorption, we need $\ell \simeq nd$, and, for n = 2, d = 1, and p = 50 torr, then S_1 and S_1' are comparable.

The "absorption efficiency" is defined as the ratio of total flux absorbed to total flux received. For the optically thin case, $n_A = n\sigma_a (IBr)d = 2 \times 10^{-2} npd$ and is much less than if $\ell \gg nd$. For the optically thick case, $\ell \ll nd$, $n_A \to 1$.

The effect of assuming σ_a was constant over an absorption bandwidth instead of being a Gaussian was investigated. The quantity $\frac{dS}{dx}$ per unit distance, where S is the rate of absorption events, was compared for the two cases. If σ_a and ϕ were constants, then $\frac{dS}{dx}$ would be proportional to $\exp[-\sigma_a(IBr)x]$. The variation of ϕ with λ and the Gaussian shape of the cross sections are shown in figure 3, where variations with temperature are also included (ref. 5). Assuming T = 300 K, a more accurate value of $\frac{dS}{dx}$ vs. x was obtained:

$$\frac{dS}{dx} = \int_0^\infty (IBr)\sigma_a(\lambda)\phi(\lambda)\,\exp[-(IBr)\sigma_a(\lambda)x]d\lambda \qquad (17)$$

The integral was performed by computer and $\phi(\lambda)$ vs. λ was stored. For the correct Gaussian cross section, at $x = \ell$, $\frac{dS}{dx}$ was about 30 percent higher than the case where σ_a was a square cross section. At $x = 2\ell$, it was twice as high for the Gaussian cross section, as less photons were absorbed from the wings where the cross section was small. Hence, in our equations, the constant σ_a should be reduced by a factor of order or less than 0.5 from the peak value assumed.

Condition for inversion. - Equations (8) and (9) can be considerably shortened if we define the ratio of He to IBr as $\alpha = He/IBr$, and assume that the amount of I_2 is determined by dissociation obeying the law of mass action. The dissociation coefficient $D = I_2/IBr$ is a function of temperature, which is known.

The quenching of Br* by IBr, He, and I_2 in equations (8) and (9) can be represented by a single coefficient k_Q:

$$k_Q = k_1 + \alpha k_2 + Dk_3 \qquad (18)$$

and the recombination of Br^* with I where both IBr and He act as third bodies can be represented by a single coefficient k_R^*:

$$k_R^* = k_4 + \alpha k_5 \tag{19}$$

Similarly, the recombination of Br and I, where both IBr and He act as third bodies, can be presented by a single coefficient k_R:

$$k_R = k_6 + \alpha k_7 \tag{20}$$

and the three exchange reactions by a single coefficient k_E:

$$k_E = k_8 + (IBr)\ [k_9 + \alpha k_{10}] \tag{21}$$

In the steady state, equations (8) and (9) become

$$S_1 = k_Q Br^* + k_R^*(IBr) \tag{22}$$

$$0 = (k_Q - k_E)\ Br^* - k_R(IBr) \tag{23}$$

It should be noted that k_Q depends on α, and the temperature T, because of the formation of I_2. The coefficients k_R and k_R^* depend on α, and may also depend on T, a behavior that will be discussed later. The exchange reaction coefficient k_E depends on the IBr pressure and on α. In addition, conservation of species exists: $I + 2I_2 = Br + Br^* + 2Br_2$.

The expression can be simplified by assuming $I_2 \simeq Br_2$ and/or that these species will be dissociated, and it therefore becomes

$$I \simeq Br + Br^* \tag{24}$$

Equations (22), (23) and (24) yield the critical value of S_1 required to make $Br^* = \frac{Br}{2}$:

$$S_1 \simeq \frac{(k_Q - k_E)\left[k_Q k_R + \frac{3}{2}(k_Q - k_E)\ k_R^*\right]}{2\ k_R^2} \tag{25}$$

We shall first consider the case where the exchange reactions are neglected and let $k_E \to 0$. If k_4, $k_5 \approx 10^{-32}$ (ref. 5), and k_6, $k_7 \approx 10^{-30}$* and k_2 is negligible,

$$S_1 \approx \frac{(k_1 + DK_3)^3}{2(k_6 + \alpha\kappa_7)} \tag{26}$$

and if $\alpha >> 1$,

$$S_1 \approx \left[\frac{(k_1 + DK_3)^2}{2k_7}\right]\frac{1}{\alpha} \tag{27}$$

The value of S_1 which is proportioned to C is reduced if $\alpha = (He)/(IBr)$ is increased. The value of S_1 is related to the concentration factor C, which must not exceed a number of around 2,000, because of overheating of the structure of the laser. From equation (12), $S_1 = nC\phi\Delta\lambda_a\sigma_a \approx 3 \times 10^{-2}C$, and this value will be approximately true in the regime when $\ell \approx d$. If we assume $k_1 = 10^{-12}$ (ref. 3) and the above values of 10^{-30} for k_3, k_6 and k_7, then with no helium, $(\alpha = 0)$, and $D \to 0$, the value of C just to achieve inversion is 5×10^6. If $\alpha = 100$, $C \approx 5 \times 10^4$. These values are much higher than experimental values for roughly the same conditions, which were $C \approx 10^4$, but the experiments were done under pulsed conditions.

If the exchange reactions are included, lower values of S_1 and C are obtained, as these reactions deplete the lower laser level. Neglecting k_R* with respect to k_R, equation (25) becomes:

$$S_1 = \frac{(k_Q - k_E)}{2k_R^2} k_Q = \frac{[(k_1 + Dk_3) - (k_8 + (IBr)(k_9 + \alpha\kappa_{10})]}{2\ k_7\ \alpha} (k_1 + Dk_3) \tag{28}$$

Now $k_Q - k_E$ has to be positive, and with the values $k_1 = 10^{-12}$, it seems unlikely that k_8 is as high as 3.5×10^{-11}. If $k_{10} = 10^{-30}$, then, at 3 torr (IBr) and $\alpha = 30$, then k_E is again comparable with k_Q, irrespective of k_8. Increasing α lowers C, and accordingly the possibility

*Values of k_4 and k_5 are assumed to be the same as for a similar reaction in I_2 taken from reference 6.

of introducing He at 10 or more times the pressure (IBr) is suggested. There are two restraints: first, if the (IBr) is at a pressure of tens of torr, then the total pressure should not exceed limits that would break the vessel; second, quenching by He may now occur. However, the intent is for He to provide more third bodies to increase the recombination rate of Br, yet not quench the Br*. The value of C would be lowered if the quenching were reduced ($C \propto k_Q^2$), and this occurs at high temperatures. Unfortunately the recombination rates are also affected, as will be seen later.

Gas Temperature in an IBr Laser

The temperature of the lasing gas can be roughly estimated assuming all the photon energy is deposited in the gas, and the heat produced is conducted to the walls of the containing vessel by gaseous conduction. The walls are at a temperature T_w and are thermally connected with a radiator into space. Above about 1,000 K, the gas would also act as a blackbody radiator.

The heat conductivity of a single gas κ is given by $\kappa = \lambda_m \bar{c} \rho C_v/3$ where λ_m is the mean free path, $\bar{c}$ is the average random velocity, ρ is the gas density, and C_v is the specific heat at constant volume of a single molecule. As $\kappa \propto \lambda_m \rho$, κ is independent of pressure. The quantity $(\lambda_m \bar{c}/3)$ is the diffusion coefficient of a molecule in its own gas, and (ρC_v) is the heat capacity per unit volume; hence, the heat conduction process is a transport of the heat content by molecular diffusion. The conduction in a mixture of gases 1, 2, 3 is due to all the species diffusing through the mixture and the effective conductivity is (ref. 7):

$$\kappa = k_1 \left[\frac{1 + a\sqrt{\dfrac{m_2}{m^1}}\ \dfrac{C'_{v_2}}{C'_{v_1}} + b\sqrt{\dfrac{m_3}{m_1}}\ \dfrac{C'_{v_3}}{C'_{v_1}} + \dots}{1 + a\dfrac{\sigma_2}{\sigma_1} + b\dfrac{\sigma_3}{\sigma_1} + \dots} \right] \tag{29}$$

Here k_1 is the conductivity of gas 1, a the ratio (gas 2)/(gas 1), b = (gas 3)/(gas 1), m = molecular weight, C_v' = specific heat at constant volume per g, and σ = elastic cross section. As $k \propto \bar{c}$, it depends on the temperature, $k \propto \sqrt{T/273}$. The conductivity of He at room temperature is 3.27×10^{-4} cal $s^{-1}cm^{-2}$ (ref. 8); that of IBr is not available, but by extrapolation from other halogens is probably about 9×10^{-6} cal $s^{-1}cm^{-2}$, a value about 300 times smaller than that of He (ref. [illegible]). Expressing the heat conductivity of an IBr-He mixture in terms of the conductivity of IBr, then at temperature T approximately:

$$\kappa \simeq 9 \times 10^{-6} \sqrt{\frac{T}{273}} \left[\frac{1 + 3.224\alpha}{1 + 5.57 \times 10^{-2}\alpha}\right] = \beta \sqrt{\frac{T}{273}} \tag{30}$$

where β is defined here. The cross section for IBr was extrapolated from that of Cl_2 (ref. 9). A plot of κ vs. α for T = 300 K is shown in figure 4.

Assuming all the heat Q deposited by the photons flows across unit area A_1 through a distance x (one-dimensional geometry), then from equation (30):

$$\frac{dQ}{dt} = \frac{A_1}{x} \beta \frac{2}{3\sqrt{273}} \left(T^{3/2} - T_w^{\ 3/2}\right) \tag{31}$$

where T is the temperature of the hot region, T_w that of the colder wall. The unit cross section A_1 is introduced because A_1/x is a parameter describing the relative distance the heat must travel (e.g., if $A_1 = 1$ cm^2, d = 1 cm, and the heat were uniformly deposited throughout the vessel of depth d, then $x \simeq d/2 = 1/2$, and $A_1/x = 2$). The treatment can be extended to several dimensions as the heat flow is a diffusion process. However, it is sufficient here to get rough estimates of what temperatures are achieved in the center of the gas. In equation (31), $\frac{dQ}{dt}$ can be expressed as the total heat deposited per unit area; if all the photons are absorbed, this is $C\phi\Delta\lambda_a\xi$ where ξ, the average energy of the photons, is approximately 5 eV. Then

$$T \simeq \left[T_w^{\ 3/2} + \frac{8.179 \times 10^{-2}C}{\beta\ (A_1/x)}\right]^{2/3} \tag{32}$$

The temperature in the center of the gas depends on T_w for which we shall assume arbitrary values, on C, $\alpha = He/(IBr)$ (which determines β), and the geometry of the laser in A_1/x. Plots of T vs. α and C were made by computer. The value α was varied from 0 to 100 and C from 0 to 2,000; increasing α serves to lower T, while increasing C raises it. Values of C required to raise T to 1,000 and 1,500 K are shown in table 1 for values of A_1/x of 1, 4, and 8--the latter achieved by cooling plates. The values of T_w chosen were 400 and 800 K. This table is for illustrative purposes only, as above 1,000 K, the gas would behave as a blackbody and radiation according to Stefan's Law would dominate. Hence, the values of C for T = 1,500 are too low.

Table 1. Approximate values of C that would raise T to 1,000 and 1,500 K (blackbody radiation neglected, α = 100).

		Value of C to Raise T to	
T_w	A_1x	1,000 K	1,500 K
400	1	150	300
	2	260	550
	4	520	1,100
	8	1,000	>2,000
800	1	~ 40	200
	2	120	400
	4	200	800
	8	400	1,600

The rough one-dimensional argument implies that very high temperatures can occur in the gas and, if C → 2000, then temperatures of well over 1,000 K should be attainable in a vessel with d = 1 cm if most of the photons are absorbed. Possible effects of such high temperatures on the laser are next discussed.

Effect of Temperature on the Rate Coefficients

General. - Temperatures can have drastic effects on quenching and recombination rates. In the case of IBr, dissociation creates I, which then forms I_2, which has a very large quenching cross section. The effect of temperature on exchange reactions is not known.

<u>Quenching</u>. - Unfortunately, experimental data on the effect of temperature on the quenching of Br* by IBr or I_2 are not available. The possible analogous case of quenching of I* by I_2 was reported by Katazaef et al. (ref. 10). They measured the quenching coefficient k_T vs. temperature and up to about 1,000 K:

$$k_T = 8 \times 10^{-11} \exp(-4.4 \times 10^{-3}T) \text{ cm}^3\text{s}^{-1} \tag{33}$$

with T in K. For example, $k_{300} = 2.14 \times 10^{-11}$, compared with a literature value of 3.6×10^{-11} (ref. 3). At 1,000 K, k_{1000} is 20 times lower. If a similar dependence occurred for the quenching coefficient of Br* by IBr or I_2, the high temperatures would prove advantageous.

<u>Thermal dissociation and formation of I_2</u>. - The amount of I_2, with its high quenching cross section, present due to thermal dissociation of IBr, is given by (ref. 10):

$$\frac{(I_2)^{1/2}(Br_2)^{1/2}}{(IBr)} = D = \frac{(I_2)}{(IBr)} \tag{34}$$

as $(I_2) = (Br_2)$. The coefficient D is obtained from the law of mass action:

$$D = \exp\left(\frac{-\Delta G}{kT}\right) \tag{35}$$

when ΔG is the free energy and k is the Boltzmann constant. The free energy has been measured (ref. 10):

$$\Delta G = -1.270 - 1.7449\ T \tag{36}$$

A plot of $(I_2)/(IBr)$ vs. T (fig. 5) shows that the ratio is 0.2 at 1,000 and 0.3 at 2,000 K. However, the conditions in the laser may be quite different because of photodissociation; the absorption cross section for I_2 is three times higher than for IBr. By including D in equation (26), the calculated S_1 will be higher--a pessimistic value. By making D = 0, with all the I_2 dissociated, the effect of I_2 can be estimated. The two cases will be compared later.

Recombination. - At 300 K the recombination rate for I + Br with a third body present is of order 10^{-30}, whereas that for I + Br* is on the order of 10^{-32} (ref. 6)--the higher energy of the Br* makes the recombination less likely.

Taylor and Rapagnani (ref. 6) have reported measurements of the recombination rates for:

$$I + I + I_2 \xrightarrow{k_6'} 2I_2$$

$$I + I + He \xrightarrow{k_7'} I_2 + He$$

The coefficients k_6 and k_7 are analogous to k_6 and k_7 used before, where I recombined with Br and the third bodies were IBr and He. These authors state that measurements of the coefficients vs. temperature showed:

$$k_6' = 1.1 \times 10^{-15} T^{-5.884} \tag{37}$$

$$k_7' = 8.3 \times 10^{-29} T^{-1.716} \tag{38}$$

The two coefficients both show a steep fall as T increases. The value of k_7' at 300 K is 4×10^{-33}, while the k_7 assumed here is 3×10^{-30}. It is apparent that more accurate numbers are required.

SPECULATIONS ON A STEADY-STATE IBr LASER

The required C for steady lasing is given by equation (25), but uncertainties in the rate coefficients make it difficult to draw conclusions. Temperatures of over 1,000 K could be easily realized, which should reduce quenching, but the recombination rates and the exchange reaction rates may also change.

If the quenching of Br^* by IBr and I_2 obeys similar laws to the quenching of I^* by I_2, then, after normalizing to room temperature values, the values would be $k_1 = 3.7 \times 10^{-12} \exp(-4.4 \times 10^{-3} T)$ and $k_3 = 8 \times 10^{-11} \exp(-4.4 \times 10^{-3} T)$. On the assumption that the quenching is reduced but that the recombination rates do not change with temperature, estimates indicate that, if C = 2,000 is a practical upper limit, then lasing should be possible for T ≈ 1,000 K, $\alpha = 100$, even if the exchange reactions are neglected.

The effect of I_2 quenching the Br^* is also estimated by assuming a dissociation which overestimates the density of I_2 when compared with D = 0. At higher temperature more I_2 is formed; nevertheless, its quenching rate is drastically reduced so the effect on the value of C is not great. The estimates are to be regarded as highly speculative as the recombination rate is assumed independent of T.

On the other hand, if the recombination rates for I + Br + IBr and I + Br + He obeyed equations (37) and (38), then steady lasing would be possible only if the exchange reactions depleted the lower level, and their dependence on temperature is not known at present.

CONCLUSIONS

The analysis of the time-varying behavior of an IBr laser seems to explain why lasing is possible under pulsed conditions, yet may be impossible in the steady state. It is apparent that care must be taken in comparing pulsed and steady-state conditions.

The inclusion of the exchange reactions lowers the calculated values of C from the values when they are neglected. Unfortunately, the rate coefficients are not known too well.

High temperatures, which are going to be unavoidable, may cause the quenching and recombination rates to vary drastically. At present, insufficient data exists on IBr to draw reliable conclusions, and there is an

acute need for reliable measurements of the rate coefficients, especially as functions of temperature. If these could be measured, then the method here makes it possible to estimate whether lasing is possible. It is speculated that if the quenching of Br* by IBr is reduced, but the recombination rates are not greatly changed, then steady-state lasing may be achieved. On the other hand, if the recombination rates behave like those of iodine, then steady-state lasing may be impossible.

It is assumed here that most of the solar radiation is absorbed and that considerable dissociation and recombination occur. Continuous flow systems should also be considered.

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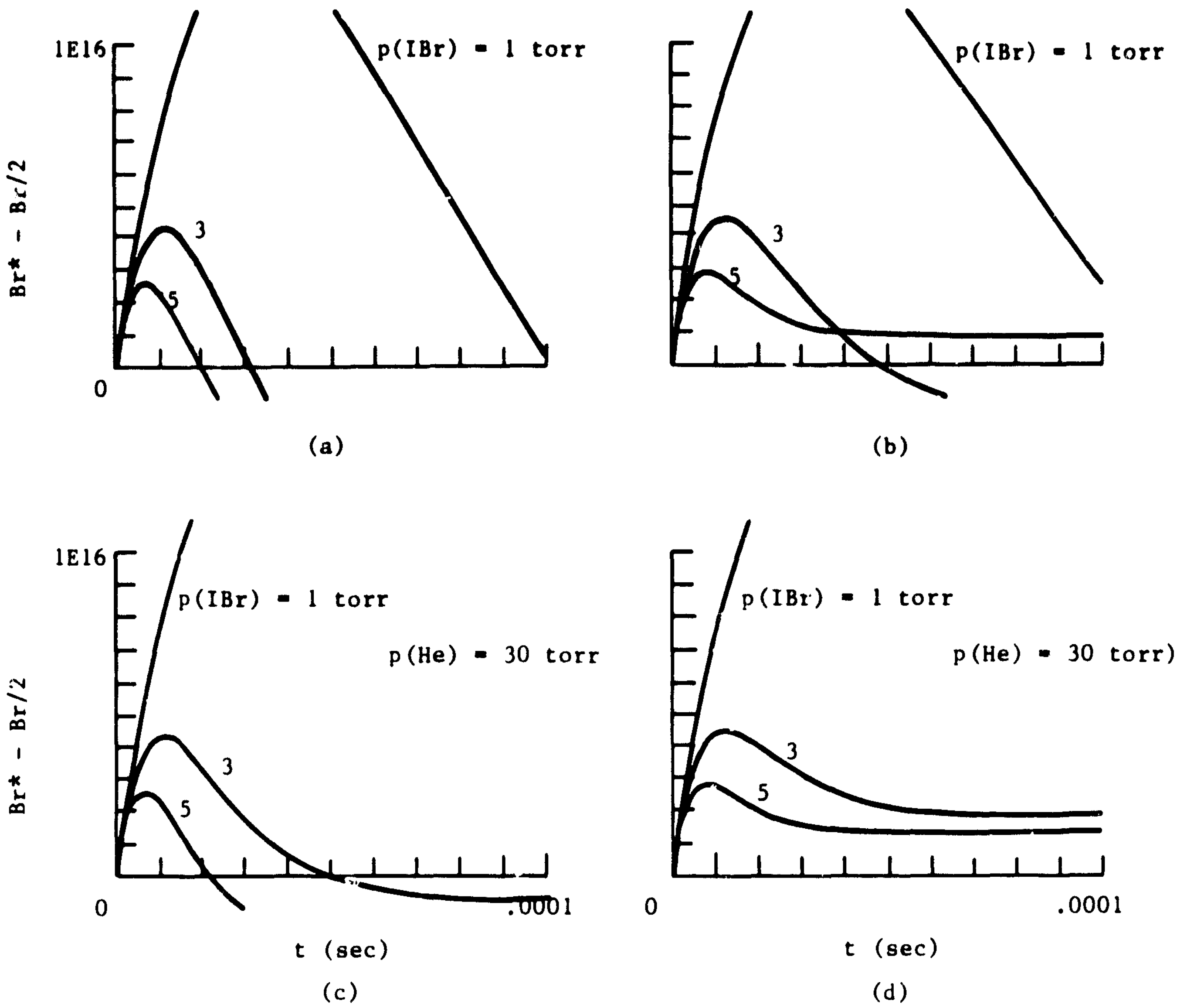

Figure 1. Plots of B_2* _ Br/2 vs. time for an IBr solar-pumped laser at pressures of 1, 3, and 5 torr. The solar concentration C = 10^4, $k_1 = 10^{-12} cm^3 s^{-1}$, $k_6 = 3 \times 10^{-30} cm^6 s^{-1}$, $k_8 = 0$. Effect of changing the value of k_9: no helium present - (a) $k_9 = 10^{-30} cm^6 s^{-1}$, (b) $k_9 = 3 \times 10^{-30} cm^6 s^{-1}$; with 30 torr He present - (c) $k_9 = 10^{-30} cm^6 s^{-1}$, (d) $k_9 = 3 \times 10^{-30} cm^6 s^{-1}$.

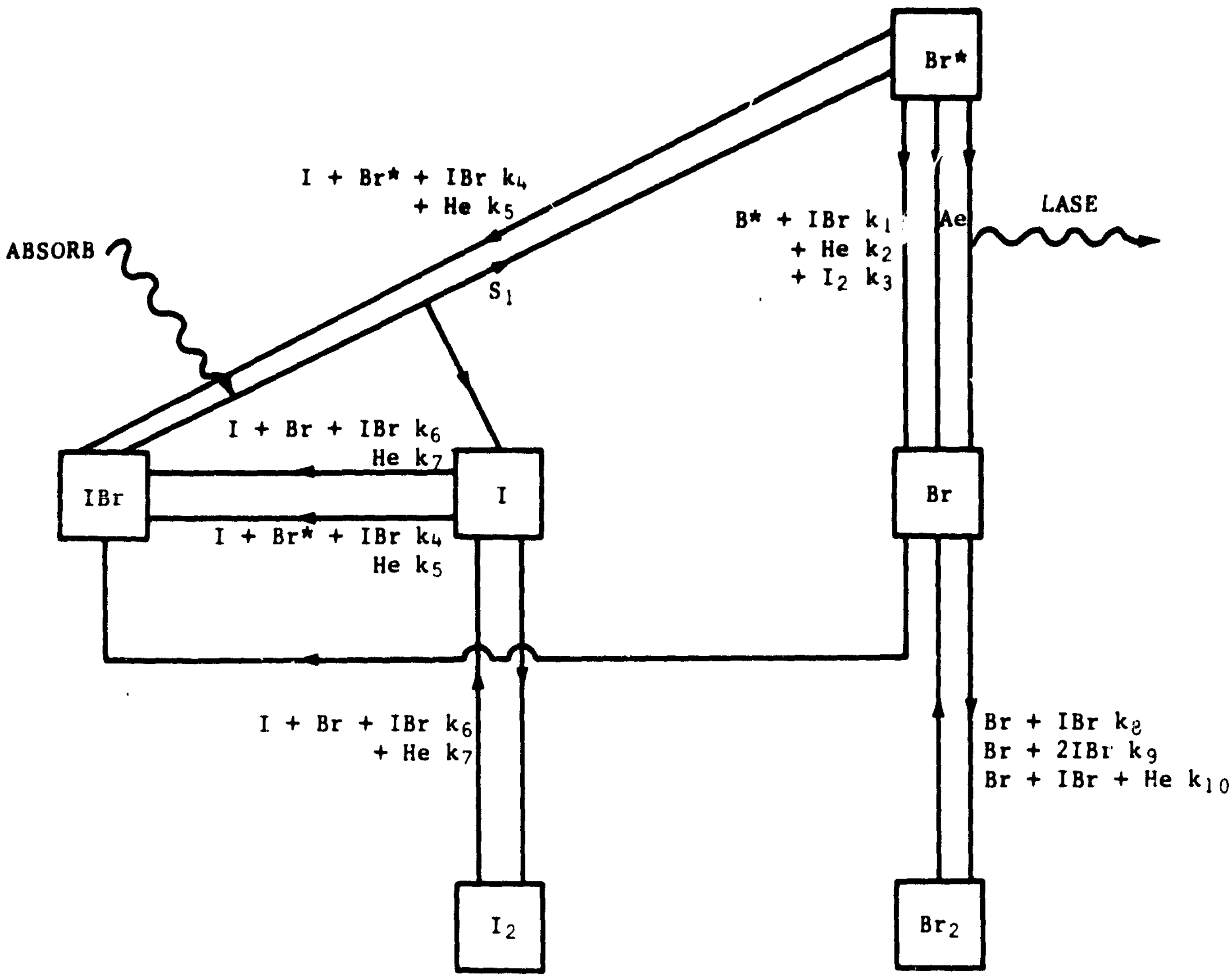

Figure 2. Flow chart for an IBr solar-pumped laser.

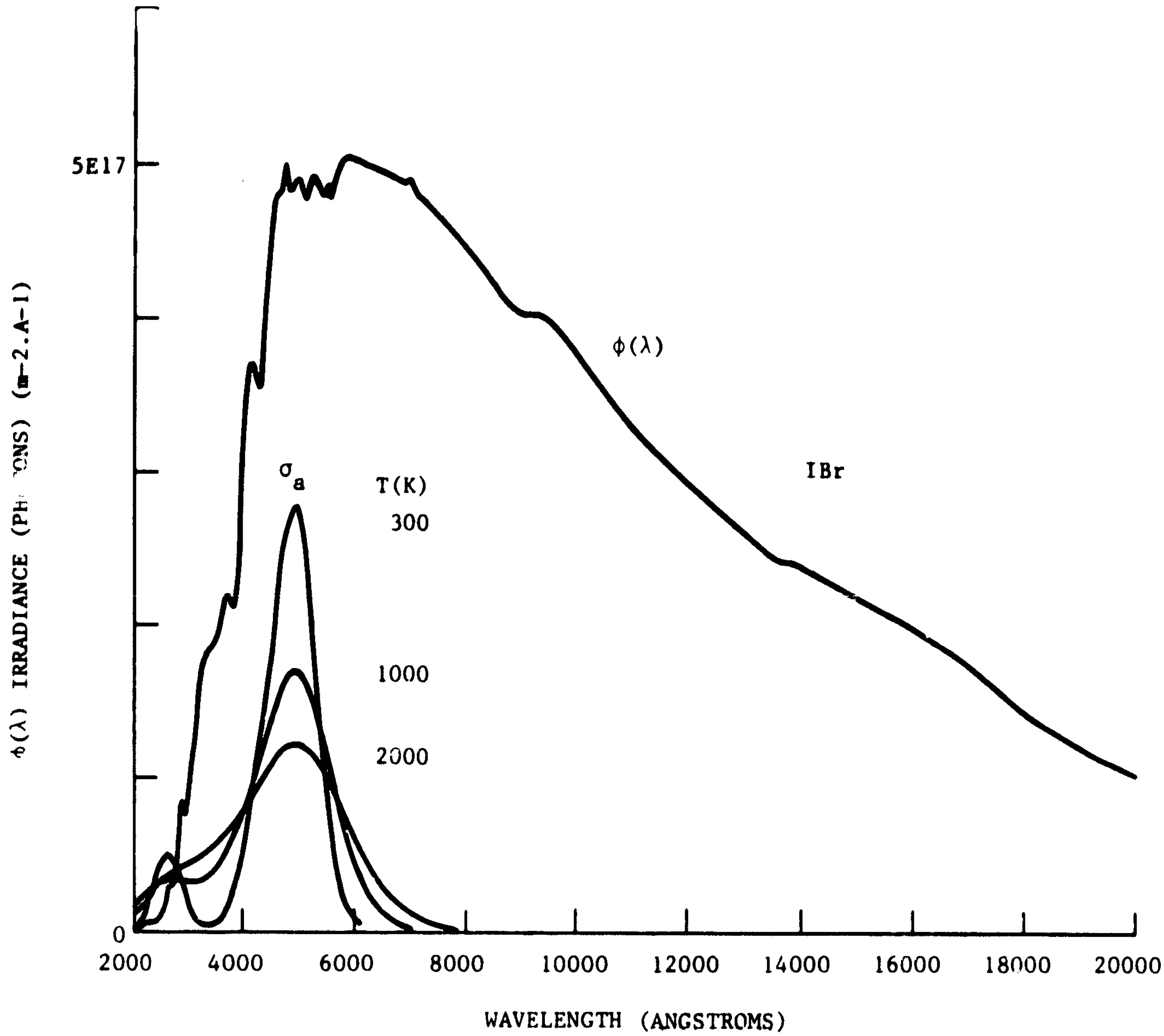

Figure 3. Plots of $\phi(\lambda)$ and σ_a vs. λ for IBr at different temperatures.

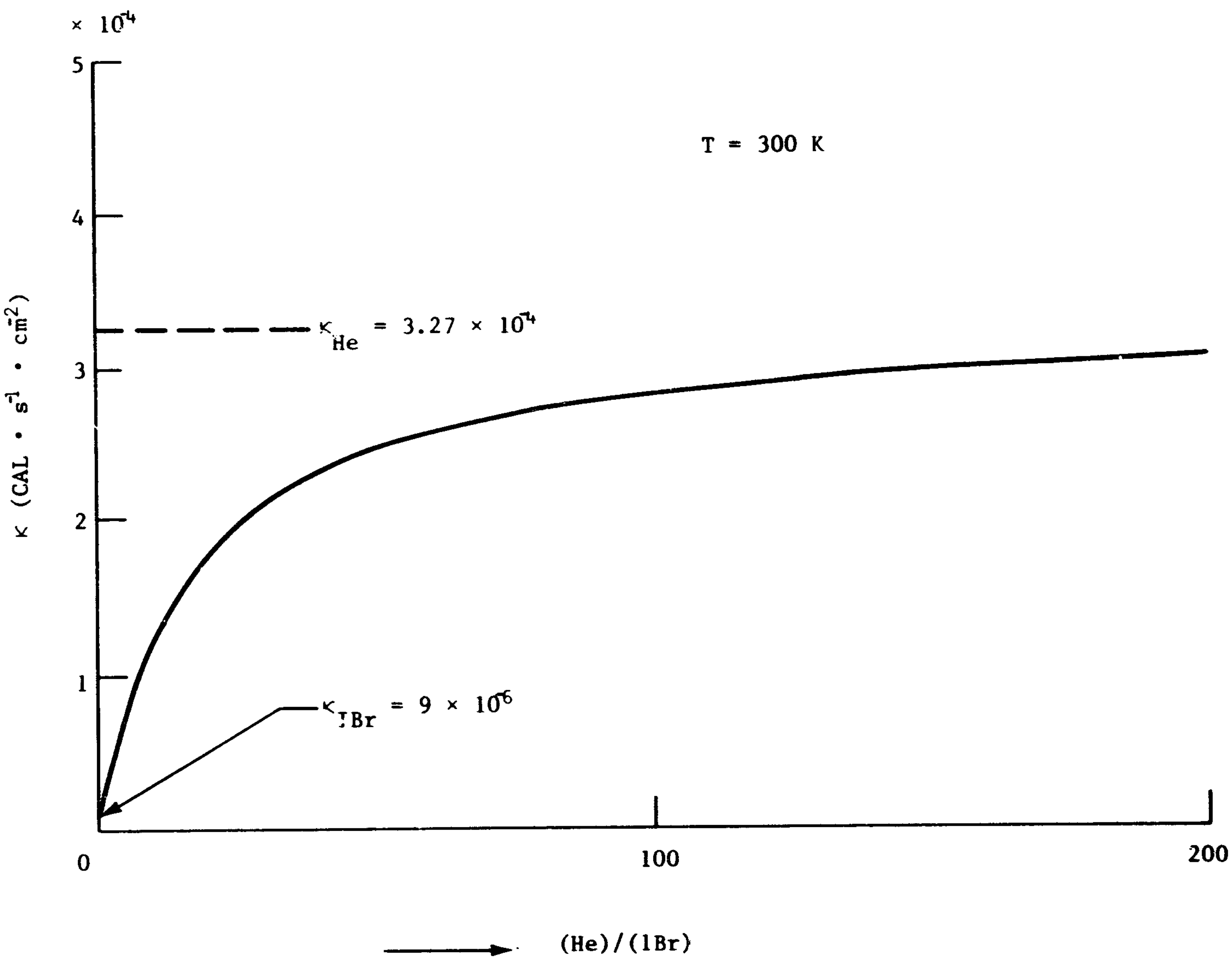

Figure 4. Plot of the heat conductivity κ of a He-IBr mixture in terms of He/IBr.

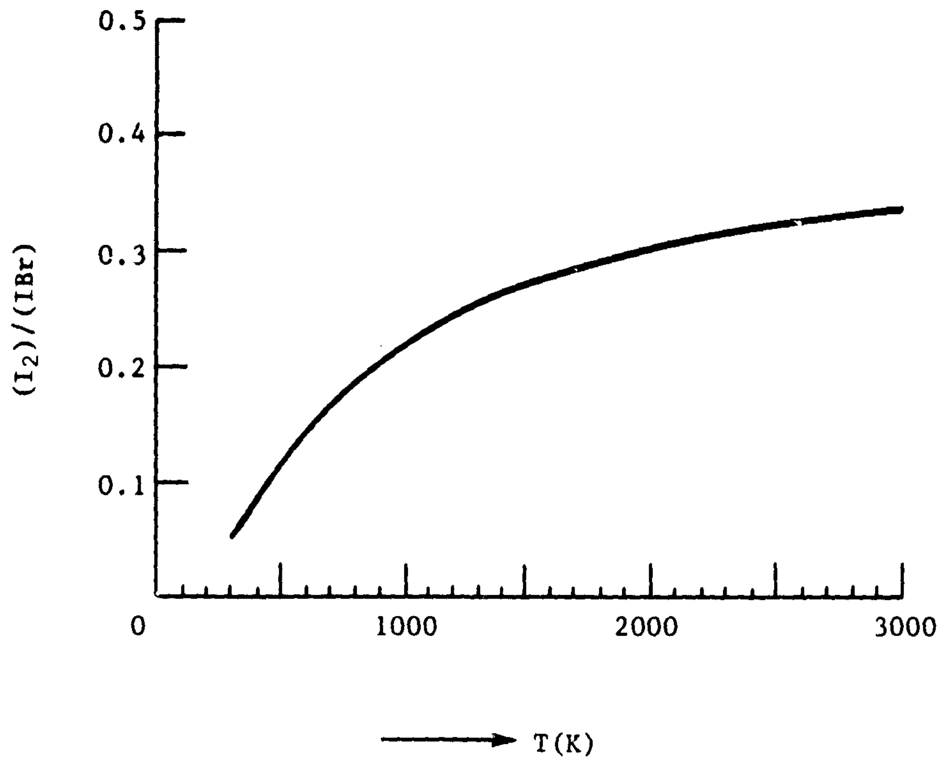

Figure 5. Plot of I_2/IBr vs. T assuming no photodissociation.